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(54) Title: A PROCESS FOR THE CATALYTIC REDUCTION OF HEAVY OILS, KEROGENS, PLASTICS, BIO - MASSES, SLUDGES, AND ORGANIC WASTE TO LIGHT HYDROCARBON LIQUIDS, CARBON DIOXIDE AND AMINES

(57) Abstract: A dendritic process encompassing 1) the con-committant hydrolysis of esters and amides, 2) the decarboxylation of the free carboxylic acids, and 3) the reductive scission of carbon-carbon carbon-nitrogen and carbon-sulfur bonds in long chain molecules is described. The process has the further encompassing simultaneous capability to confine / concentrate contaminant metals to specific separated fractions and to reduce the overall sulfur contents therein and when triglycerides are present to help desiccate the hydrocarbon fraction.

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TITLE:

A PROCESS FOR THE CATALYTIC REDUCTION OF HEAVY OILS, KEROGENS, PLASTICS, BIO-MASSSES, SLUDGES AND ORGANIC WASTE TO LIGHT HYDROCARBON LIQUIDS, CARBON DIOXIDE AND AMINES OF WHICH THE FOLLOWING IS THE SPECIFICATION.

Specifications / Background of the Invention

The ideal dendritic process, as described by Paul A Wender [ACS Chemical & Engineering News page 27 01 08 2001] 1) has the capability to use readily available, diverse sources, low cost, mixed raw material, 2) has a short cycle time, 3) has a net positive energy balance, 4) requires no solvent, 5) has robust process variables and a) is multi-stepped in one reaction vessel, b) leaves no environmental footprint and c) generates controllable purified separated products in 100% yields while involving as few personnel and as little equipment as possible.

By *dendritic* is meant a simultaneous / all at once set of multi-stepped reactions, separations and isolation of purified streams of targeted variable products from raw material constituents in a single stage reaction vessel. An example is found in Canadian Patent 2249110. Others are described by C.R. Strauss in the Australian J. Chemistry 52 83-96 (1999) and J. Haggin in Chemical and Engineering News 74 (23) 38 (1999).

The major constituents of 1) biosynthetic plant/animal tissue and 2) geo/ man made polymers are carbohydrates, lignin, waxes, lipids, proteins, kerogen, mineral oils and plastics.

The three states of matter are solids, liquids and gases. Depending on pressure and temperature the three phases can exist singly or in equilibrium with other phases. Water has, what is known as, three "co-existence curves". They consist of a solid / gas equilibrium called the sublimation curve, a liquid / gas equilibrium called the vapour pressure curve, and a solid / liquid equilibrium called the melting curve. There also exists a triple point where all three phases exist in equilibrium. The point on the vapour-liquid curve where the liquid and vapour become identical is called the critical point. The temperature at this point is called the "critical temperature" ($T_{sub.c}$ water = 374°C) and the pressure is called the "critical pressure" ($P_{sub.c}$ water = 218 atmospheres). O. Maass and E.W.R Steacie. *An Introduction to the Principles of Physical Chemistry* pages 80-83 John Wiley and Sons Inc. 1939 ; <http://www.kobelco.co.jp/p108/p14/sfe01.htm>

No gas can be liquefied above its T.sub.c. As water is heated under pressure, it slowly begins to lose its H-bonding characteristics, act more and more like a lower dielectric constant solvent and become less dense. Above its T.sub.c / P.sub.c supercritical water (SCW) has a dielectric constant of less than 5 and a density of 0.2 gm / ml. Hence, SCW as a supercritical fluid simultaneously acts both as a liquid and a gas with the solvent power of an organic liquid such as benzene.

Classic organic reactions such as hydrolysis, bond cleavage and bond formation can occur in the sub-critical zone as described by Wideman L.G. et al *USPat 4515713*; Lesutis H.P. et al *Chem. Commun.* 1999, 2063, and at or above the super critical temperature of water. B. Kuhlmann, E.M.Arnett, M. Siskin *J. Org. Chem* 1994, 59, 3098-3101 C.R.Strauss *Aust. J. Chem.* 1990, 52, 83-96.

Ester, thioester and amide hydrolysis is usually accompanied by decarboxylation in SCW. The following patents respectively teach the use of acid, basic and neutral catalysts in such reactions: Zeiler, A.C. *USPat. 5344975*, Theriot, K.J. et al. *USPat. 5329054*, and Sealock, L.J. et al. *USPat. 5630854*.

Carbon - carbon and carbon - sulfur bond rupture followed by hydrogenation of the terminal ionic or free radical end is thermal hydrocracking [Gray M.R. et al. *Energy and Fuels* 6(4) 478-485 1992] and / or hydro-desulfurization [Whitehurst D.D. et al. *Adv. Catal.* 42 345 (1998)]. Patel, K.M. et al. *USPat 4743357* teach the conversion of heavy hydrocarbons into light hydrocarbons by water and an effective amount of selected catalyst material such as iron (II and/or III) oxides, sulfides or sulfates in the absence of externally added hydrogen; at a temperature greater than 340.degree. and less than 480.degree.C. Pyrolysis without hydrogenation generates coke. Examples of coking are found in the thermal generation of methane gas, distillates and coke when pyrolyzing coal and wood. An excellent reference is found at <http://www.newcastle.edu.au>.

Amino acids under oxidative reaction conditions are known to denitrify. The products of the Akabori (*J. Chem. Soc. Japan* 52, 606 (1931)), van Slyke (*J. Chem. Soc.* 99, 792 (1911)) and Strecker (*Annalen* 123, 363 (1862)) reactions are aldehydes, ammonia and carbon dioxide. We detected ammonia, carbon dioxide, phenethyl amine and a tar when subjecting phenyl alanine to SCW conditions at 430.degree.C.

The array of products generated when subjecting reactants to SCW conditions, is separated by capture of gases, condensation of liquids in a distillation tower and crystallization / precipitation of solids. Examples of capture of gases are precipitation of carbon dioxide by lime, formation of amine salts by acids and condensation of low boiling hydrocarbons by cryogenic means.

An example of a distillation tower partitioning is the separation of gases and liquids of differing boiling points from each other. The accompanying table presents an example of hydrocarbon boiling ranges for a distillation tower.

Carbon Chain Length	Class	Boiling Point Range, degree. C
C.sub.5-C.sub.10	Gasoline	37 - 175
C.sub.10-C.sub.15	Kerosene/Jet Fuel	175-275
C.sub.12-C.sub.20	Diesel	190-330
C.sub.14-C.sub.22	Fuel Oil	230-360
C.sub.20-C.sub.30	Lubricating Oil	>350
C.sub.22-C.sub.40	Petroleum Jelly	40-60 (m. pt.)
C.sub.25-C.sub.50	Paraffin Wax	50-65(m.pt.)
C.sub.50+poly cyclics	Tar/bitumen	> 400

Aqueous glycerol solutions are known to be insoluble in hydrocarbons. [*The Merck Index Entry 4493 ISBN # 0911910-1-2-3 (1996)*]. Diaz Z and Miller JH [USPat 4478612] teach the use of glycerol as a water-binding astringent in supercritical carbon dioxide.

SUMMARY DESCRIPTION OF THE INVENTION

One Step Dendritic Process

This invention relates to the reaction of variegate raw materials and the separation and isolation of the products. The invention takes advantage of the reduction in the number of profligate process steps, the cycle time for the reaction and the capacity to separate the products using a dendritic process.

An example follows. A mixture of nylon 6, nylon 6,6, nylon 6,10 and nylon 6,12 is subjected to a high temperature in the presence of SCW. Hydrolysis of the nylons produces a mixture of ω -amino caproic acid, 1,6-diamino hexane, hexan-1,6-dioic acid, decan-1,10-dioic acid and dodecan-1,12-dioic acid. Decarboxylation of the amino acid and the diacids generate fractionally distillable carbon dioxide + pentyl amine + 1,6-diamino hexane + butane + octane + decane. The amines are catalysts for the reactions. Other known catalysts such as acids, bases and iron oxides embedded in an alumina-silica matrix can be added to the reaction vessel. Hence in one reaction

vessel, water is consumed and a mixture of four nylons generates two amines, three hydrocarbons and carbon dioxide.

Another example follows. Polyethylene is subjected to a high temperature in the presence of water and iron oxide embedded in an alumina-silica matrix or a basic catalyst such as sulfide. Reductive thermolytic cleavage of carbon-carbon bonds and oxidation of the sulfide to sulfate ion gave C.sub.22 to C.sub.40 waxes or fractionally distillable C.sub.10 to C.sub.22 hydrocarbons respectively. Hence in one reaction vessel, water is consumed and a mixture of hydrocarbons is formed.

Still another example follows. A mixture of variegate source triglycerides and lipids (preferably with some protein contaminant) of animal and/or vegetable origin is subjected to a high temperature in the presence of water, with or without a catalyst. Hydrolysis of the proteins produces a mixture of amino acids. Hydrolysis of the triglycerides and lipids produces a mixture of C.sub.4 to C.sub.24 carboxylic acids plus glycerol. Decarboxylation of the amino acids and the carboxylic acids generate fractionally distillable carbon dioxide, amines, ammonia and C.sub.3 to C.sub.23 hydrocarbons. The amines and ammonia are catalysts for the reactions. Other known catalysts such as acids, bases and iron oxides embedded in an alumina-silica matrix can also be added to the reaction vessel. Concomitant deamination and decarboxylation of the amino acid generate aldehyde, carbon dioxide and free ammonia. A further embodiment of this example is that glycerol is a desiccant for the generated hydrocarbons and absorbent for the ammonia. Thus the dry hydrocarbon phase can be separated before fractional distillation is carried out. Hence in one reaction vessel, water is consumed and a mixture of triglycerides, lipids, and protein is converted to amines, ammonia, desiccated hydrocarbons, glycerol and carbon dioxide.

Yet another example follows. Animal excrement and vegetable wastes that have a fair proportion of triglycerides, lipids and protein is subjected to a high temperature in the presence of water, with or without a catalyst. Hydrolysis of the proteins produces a mixture of amino acids. Hydrolysis of the triglycerides and lipids produces a mixture of carboxylic acids plus glycerol. Decarboxylation of the amino acids and the carboxylic acids generate fractionally distillable carbon dioxide, amines, and C.sub.3 to C.sub.23 hydrocarbons with little, if any, methane gas (*Sealock Jr. L.J. et al USPat 5630854* teach the generation of methane gas only). The amines are catalysts for the reactions. Concomitant de-amination and decarboxylation of the amino acid generate aldehyde, carbon dioxide and free ammonia. Other known catalysts such as acids, bases and iron oxides embedded in an alumina-silica matrix

can also be added to the reaction vessel. A high proportion of protein naturally generates a higher ratio of amines to hydrocarbons. Capture and isolation of the putrid smelling amines and ammonia ensures an odour free process and nitrogen reduced residue. Solid insoluble coke residue (poly saccharide derivation) and mineral salts are also obtained. Hence in one reaction vessel, water is consumed and human, swine, and bovine excrement is converted to carbon dioxide, amines, ammonia, hydrocarbons, glycerol, and nitrogen-depleted carbonaceous compost. This odour/pathogen free residue can be used as a low-grade fuel or compost. A further example follows. Lake Asphalt Tar Sand that has a fair proportion of carboxylic acids is subjected to a high temperature in the presence of super critical water and 20% by volume used vegetable oil. Hydrolysis of ester content and decarboxylation of the total acids plus reductive cleavage of high molecular weight hydrocarbons followed by separation of the solids by centrifugation generated a distillable (160 – 220.degree. C) hydrocarbon fraction and a fraction whose boiling point was greater than 220.degree. C. Solid insoluble residue (mineral salts) with an organo-sulfur contaminated tar is also obtained. Hence in one reaction vessel, water is consumed and tar sand plus vegetable oil is converted to carbon dioxide, hydrocarbons, glycerol and residual tar contaminated clay.

An additional example follows. Heavy oils that have been doctored with waste lipid oil (as a processing aid in the pipeline transport of crude) are subjected to a high temperature in the presence of SCW. Hydrolysis of the esters, decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons generated fractionally distillable desiccated lighter hydrocarbons, physically separable water-loaded glycerol and filterable solids. The solid insoluble residue contained mineral salts and very heavy tars. Hence in one reaction vessel, water is consumed and lipid doctored heavy oil is converted to carbon dioxide, hydrocarbons, and residual contaminant (V-Ni-Fe) metals.

A still additional example follows. Waste canola vegetable oil was subjected to a 500.degree. C temperature in the presence of SCW. Hydrolysis of the esters, decarboxylation of the acids and thermal cleavage of generated hydrocarbons gave fractionally distillable desiccated lighter hydrocarbons, physically separable water-loaded glycerol and a filterable residue. Hence in one reaction vessel, water is consumed and vegetable oil is converted to carbon dioxide, glycerol and hydrocarbons.

A next to final example follows. Albert shale from Stoney Creek New Brunswick was subjected to a high temperature in the presence of SCW. Reductive thermolytic

cleavage of carbon-carbon bonds gave C.sub.12 to C.sub.26 hydrocarbons as determined by GC/MS.

A final example follows. Extracted lignin or black liquor from the Kraft (sulfide + carbonate) and Soda-AQ (carbonate) process was subjected to super critical temperatures. Hydrolysis of the esters, decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons generated fractionally distillable hydrocarbons and physically separable precipitated carbonaceous solids. The separated aqueous fraction from the Kraft process contained a mixture of carbonate and sulfate ion. Trace sulfide ion was found. Hence in one reaction vessel, water is consumed and pulp black liquor is converted to carbon dioxide, hydrocarbons, carbonaceous fuel and green liquor without resorting to an energy intensive five stage evaporation in order to concentrate the black liquor.

This makes the environmentally more friendly Soda-AQ process more financially competitive than the Kraft-Sulfide process since the Soda-AQ carbonate need not be raised to 1200.degree.C in order to convert sulfate to sulfide.

DETAILED DESCRIPTION OF THE PROCESS

In accordance with the present invention, a pressurized aqueous system is used for the transformation of higher molecular weight organic compounds into lower molecular weight hydrocarbons of reduced viscosity. The invention provides two methods for reducing the viscosity of organic raw materials. The first is by converting, 200-300.degree.C sensitive esters, thioesters, amides, and amino acids to "one carbon shorter" hydrocarbons and/or amines. The second is by thermolytic cracking of the more labile carbon-carbon and carbon-sulfur bonds at 400-500.degree.C. Distillation is used to separate the lower viscosity constituents from each other. The combined inorganic phase and metal-tar contaminants separation is achieved by centrifugation.

The process of this invention can be conducted in batch or continuous fashion, with recycle of unconsumed starting materials, if required. The reaction is conducted in a single reactor zone. The materials of construction employed should be inert to the starting materials, intermediate reaction materials and the final products for the reaction process. The fabrication of the equipment should be able to withstand the reaction temperatures and pressures.

The present invention is a method for converting organic materials into lower molecular weight hydrocarbons. This is accomplished by injecting an organic raw material in the form of an aqueous mixture, preferably 10-50% by weight through a

sixteenth inch tube. The amount of water present must be sufficient to provide hydrogen as needed to promote the formation of reduced hydrocarbons. A stirrer in the starting materials reservoir agitates the aqueous mixture of organic raw materials, water and catalyst. A pump that feeds the raw material to the reactor can generate a pressure of 200-250 atmospheres. The pressurized raw material is preheated to minimum 250.degree.C by means of a heat exchanger before entry into the reactor. The reactor mass is maintained at a temperature of 400-525.degree.C, preferably 430-500.degree.C, as predetermined by TGA/MS analysis of the reaction raw material and a pressure that is commensurate with the temperature. An electric heater heats the autoclave with the capability to maintain the temperature of the twenty-foot length, sixteenth-inch diameter reactor-tube at approximately 500.degree.C. The system is provided with a cooling coil as it exits the autoclave area. Recovered energy is used to preheat fresh raw material as it enters the autoclave reaction chamber. Gas and liquid samples are taken after completion of the reaction and cool down.

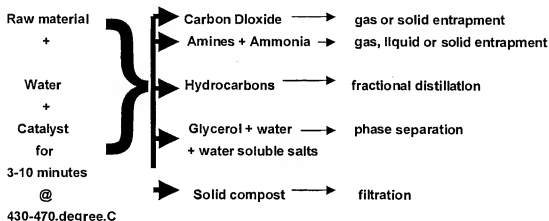
In preferred embodiments of the inventions the following proportions of components can be used.

Experiment 1 – Continuous Process Mode.

Trimmed pork fat including rind and residual flesh, which is not limiting to the animal raw materials that can be used in the process, is pulped. To the pulped fat is added water such that a 50% by weight fat to water mixture is prepared. Pulped pig fat is pumped to the reactor at a rate of 300 ml/hour under 218 atmospheres of pressure. The pressurized pulp is preheated to 250.degree.C by means of a heat exchanger before entry into the reactor. The reactor is maintained at a temperature of 470.degree.C. Hydrolysis of the triglycerides and proteins with sequential decarboxylation of the freshly generated carboxylic acid functional groups and possible oxidation of the free amine occurs in the twenty-foot length, sixteenth-inch diameter reactor-tube. Generated amine and ammonia provides a catalytic effect for the hydrolysis reaction and anti corrosive protection of the walls of the reactor. Energy recovered on cooling the exiting autoclave products is used to preheat fresh raw material as it enters the autoclave reaction chamber. Gas, liquid and solid products are refined as described below. The fractionally distilled (less than 220.degree.C) product of the reaction by Gel Permeation Chromatography was mainly C.sub.13, C.sub.15, and C.sub.17 alkanes, and glycerol. GC/MS confirmed the presence of C.sub.13, C.sub.15, C.sub.17 alkanes, and carbon dioxide. A second

experiment at 500.degree.C caused thermal cracking. GC/MS showed the presence of C.sub.7 to C.sub.14 alkenes plus C.sub.7 to C.sub.17 alkanes.

DENDRITIC REACTION PROCESS



By solid entrapment is meant bubbling the gas fraction of the reaction mixture first through an acid solution (generates ammonia and amine salts) and then through a lime solution (precipitates calcium carbonate). Glycerol is a strong water astrigent. Water laden glycerol is hydrocarbon insoluble and forms a separate phase. Distillation of the hydrocarbon phase shows no trace of water present. Skin, ligament and some protein fractions of the pig fat carbonize under the reaction conditions. Physical filtration of the solids from the liquid phases provides solid compost that can be applied to the land as soil builder or burned as a fuel.

In another preferred embodiment of the invention the following proportions of components can be used.

Experiment 2- Continuous Process Mode.

Partially de-watered pig excrement including floor washings, which is not limiting to the excrement source that can be used in the process, is prepared as a less than 20% by weight solids mixture. A pump feeds the conditioned excrement to the reactor at a rate of 300 ml/hour under 218 atmospheres of pressure. The pressurized excrement is preheated to 250.degree.C by means of a heat exchanger before entry into the reactor. The reactor is maintained at a temperature of 430.degree.C. Hydrolysis of the triglycerides and proteins with sequential decarboxylation of the freshly

generated carboxylic acid functional groups (partial oxidation of the liberated amino acid is possible) occurs in the twenty-foot length, sixteenth-inch diameter reactor-tube. All pathogenic material is sterilized and becomes part of the raw material. Generated amine and ammonia provides a catalytic effect for the hydrolysis reaction and anti corrosive protection of the walls of the reactor. Energy recovered on cooling the exiting autoclave products is used to preheat fresh raw material as it enters the autoclave reaction chamber. Gas, liquid and solid products are refined as described in experiment 1. The amine fraction is composed of ammonia from glycine; methyl amine from alanine, aspartic acid, asparagine and β -alanine; dimethyl amine from sarcosine; trimethyl amine from betaine; iso-butyl amine from valine; iso-pentyl amine from leucine; ethanol amine from serine; 1,2-propanol amine from threonine; 1,3-propanol amine from homo-serine; putrescine from lysine, arginine, and ornithine; histamine from histidine; phenethyl amine from phenyl alanine; tyramine from tyrosine; tryptamine from tryptophan; cysteamine from cysteine; pyrrolidine from proline.

Amines are odiferous compounds that are usually associated with excrement and decomposing proteins. Putrescine (1,4-diamino butane) and cadaverine (1,5-diamino pentane) aptly derive their nomenclature from the latin – putere or putrefaction and cadere or cadaver. Isolation and containment of the amines is one way to achieve abatement of foul odours. Partial oxidation of the amino acids to aldehyde and ammonia gave an aqueous solution containing 13.9g/l N-NH.sub.3, a Total Kjeldahl Nitrogen of 15.1g/l, trace N-NO.sub.2, trace N-NO.sub.3, 29.0g/l Potassium and 1.11 g/l Total Phosphorous. The low phosphorous content in the aqueous phase is indicative of insoluble phosphates in the residual solids. Attempted deamination of free amine using SCW was unsuccessful.

In still another preferred embodiment of the invention the following proportions of components can be used.

Experiment 3 - Continuous Process Mode.

Twenty percent by weight waste cooking oil (which is not limiting to the amount of triglycerides that can be used in the process) was added to the heavy-oil bottoms asphaltene fraction separated from Kern River crude. The viscosity reduced mixture is preheated to 250.degree.C by means of a heat exchanger before being pumped into the reactor at a rate of 300 ml/hour under 218 atmospheres of pressure. The reactor was maintained at a temperature of 430.degree.C. Hydrolysis of the triglycerides and tramp proteins with sequential decarboxylation of the freshly generated carboxylic

acid functional groups occurred in a twenty-foot length, sixteenth-inch diameter reactor-tube. Generated amine provided a catalytic effect on the hydrolysis reaction. Energy recovered on cooling the exiting autoclave products is used to preheat fresh raw material as it enters the autoclave reaction chamber. Gas, liquid and solid products were refined as described above. The distillable hydrocarbon, which was not present in the starting raw materials, had a boiling point range fraction of 160 - 220.degrees.C

In yet still another preferred embodiment of the invention the following proportions of components can be used.

Experiment 4 - Continuous Process Mode

Waste canola vegetable oil was subjected to a 500.degree.C temperature in the presence of SCW. Hydrolysis of the esters, decarboxylation of the acids and thermal cleavage of generated hydrocarbons gave fractionally distillable desiccated lighter hydrocarbons, physically separable water-loaded glycerol and a filterable residue. The fraction, which distilled between 60 and 220.degree.C was shown by GC/MS to contain C.sub.4 - C.sub.15 alkanes and alkenes. Trace amounts of C.sub.10 and C.sub.11 alkyl benzene was also detected. The non-distilled fraction above 220.degree.C was shown by FTIR to contain free acid (1710 cm.sup.-1) and no starting material (1736 cm.sup.-1).

Preliminary experiments were carried out in a batch reactor. The reactor was constructed from a six-inch diameter stainless steel rod of seven-inch length. Eight half-inch diameter bolts were used to hold a cover head in place. A copper gasket was used to maintain an ultimate pressure of 250 atmospheres in the 40 ml volume well of the reactor. Six propane torches were used to heat the reactor to 430-470.degree.C. Ice was used to cool the reactor once the reaction temperature was reached.

Experiment 5 Batch Process Mode

To 40 grams of Trinidadian Lake Asphalt Tar Sand (70% by weight clay) was added 15 ml of water. The temperature of the reactor was raised to 430.degree.C. Upon reaching 430, the source of heat was shut down and cooling was started. Upon reaching room temperature the reactor was opened. Trapped carbon dioxide escaped. The oily-water residual material was extracted with methylene chloride. The extract gave a heavy oil that boiled above 200.degree.C. The residual clay contained

3% by weight tar. The aqueous phase contained trace amounts of sulfide (0.08 mg/l) and large amounts of sulfate (288mg/l).

Experiment 6 - Batch Process Mode

To 20 grams of 57% aqueous butoxyethanol insoluble Athabasca heavy oil (i.e. maltene extracted asphaltene residuum; Number average molecular weight by Gel Permeation Chromatography 413; Polydispersity 3.78; Molecular range ~400 - 10000) was added 15 ml of water and 100 mg aspartic acid. The temperature of the reactor was raised to 430.degree.C. Upon reaching 430, the source of heat was shut down and cooling was started. Upon reaching room temperature the reactor was opened. Trapped carbon dioxide and amine/ammonia escaped. The oily-water residual material was partitioned using 100ml 20% by volume butoxyethanol in water at 80.degree.C. All of the viscosity-reduced oil dissolved in the top layer (57% butoxyethanol in water) and a solid residue collected at the bottom of the 10% butoxyethanol in water layer. The viscosity-reduced oil had a number average molecular weight of 277; Polydispersity 1.62; Molecular range ~100 - 1500 and a 17.37, 2.29 and 1.53 fold decrease in Iron, nickel and vanadium respectively. The mostly carbon solid residue had much higher concentrations of Iron, nickel, and vanadium.

Experiment 7 Batch - Process Mode

Crude light (Brut/Isthmus/Maya -35ml) oil that had a naphthenic acid portion was subjected to a high temperature in the presence of SCW with an amino acid catalyst causing decarboxylation of the acids and reductive cleavage of higher molecular weight hydrocarbons. The starting density of the oil was 0.8923 g/ml at 20.degree.C; the final density was 0.8633. Solid insoluble residue contained most of the V-Ni-Fe metal.

Experiment 8 Batch - Process Mode

To 20 grams of low density polyethylene film was added 0.5 gm sodium sulfide and 15 ml of water. The temperature of the reactor was raised to 460.degree.C. Upon reaching 460, the source of heat was shut off and cooling was started. Upon reaching room temperature the reactor was opened. The oily-water residual material was partitioned from the aqueous phase using 100ml-methylene chloride. Filtering it through a pad of basic aluminum oxide decolorized the methylene chloride solution. The kerosene smelling light oil was tested for sulfur content. Analysis showed the oil contained 0.1% sulfur. The water phase was also analyzed for sulfide and sulfate content. Greater than 98% of the sulfide had been converted to sulfate. A repeat

reaction using 7.5% ferric oxide on alumina silicon dioxide as catalyst gave a waxy hydrocarbon product. The melting point was 25-30.degree.C.

Experiment 9 – Batch Process Mode

To 25 grams of crushed Albert Shale (20% organic content) from New Brunswick Canada was added 10 mls of water. The temperature of the reactor was raised to 460.degree.C. Upon reaching 460, the source of heat was shut down and cooling was started. Upon reaching room temperature the reactor was opened. The oily-water residual material was partitioned from the aqueous phase using 100ml methylene chloride. Oil was obtained upon evaporation of the solvent. GC/MS analysis indicated that the oil was composed of C.sub.12 to C.sub.26 saturated hydrocarbon.

Experiment 10 – Batch Process Mode

35 mls of used lubricating oil (a mixture of motor oil, grease, transmission oil, gasoline, ethylene glycol, water, floor sweepings, etc.) was placed in the reactor well. The temperature of the reactor was raised to 430.degree.C. Upon reaching 430, the source of heat was shut down and cooling was started. Upon reaching room temperature the reactor was opened. The oily-water residual material was gravity fed through an S&S qualitative No. 410 filter paper. Water remained in the oil-residue impregnated filter paper. The coloured oil filtrate was gravity fed through a ten centimeter long one cm diameter pad of dry Brockmann I, ~150 mesh basic alumina in order to remove all colour.

ICP analysis of the water white oil showed the following metals to be less than 1 ppm: aluminium, arsenic, barium, boron, cadmium, calcium, chromium, copper, iron, lead, magnesium, molybdenum, nickel, phosphorous, selenium, silicon, silver, sodium, tin, titanium, vanadium, and zinc.

Experiment 11 – Batch Process Mode

35 mls of 18% Kraft black liquor (sulfide-soda) was placed in the reactor well. The temperature of the reactor was raised to 430.degree.C. Upon reaching 430, the source of heat was shut down and cooling was started. Upon reaching room temperature the reactor was opened. The oily-water residual material was partitioned from a solid phase using 100 ml methylene chloride. Viscous oil was obtained upon evaporation of the dried methylene chloride solvent. GC/MS analysis indicated that the oil was composed mostly of polyaromatic material. Solid powered carbonaceous material (Total Organic Carbon = 43.9%) was filtered from the reaction mixture. Examination of the water showed that all of the sulfide ions had been oxidized to sulfate and that most of the lignin reaction products had been precipitated out. Upon standing, the

water white aqueous phase began to take on a brown colour – most likely oxidation of water-soluble phenolics.

Treatment of 18% Soda-AQ black liquor under the same conditions gave a greater yield of lower boiling point range hydrocarbon and a slightly lesser yield of carbonaceous material.

ADVANTAGE OF OUR PROCESS

1. Simplicity of the equipment and the process requiring fewer personnel	Low capital costs, maintenance fees and salaries.
2. One step dendritic separation of the organic, water soluble and solid inorganic constituents	Smaller portable reactors with short cycle times.
3. Performing the reaction and separation of constituents in one step.	Eliminating the costs of profligate process steps.
4. Can use readily available, diverse mixed-source raw material	Security against availability of raw materials sources and prices.
5. Reduction in the viscosity of the heavier oil fractions	Increased pipeline flow capabilities at lower temperatures.
6. Up-grading the constituents by concentrating metals into fewer product streams.	Reduction of the oil volumes which require de-contamination treatment.
7. Reducing odour producing organosulfur and nitrogen compound products	Eliminates catalyst poisoning; Lowers treatment costs, increases social acceptance
8. Increases liquid volume yield	Decreases coke yield.
9. Provides a drying agent when glycerol is generated	Eliminates emulsion formation
10. Reduces the energy cost to delignify cellulose pulps. Raises the cost competitiveness of the Soda-AQ process	Provides an alternate recovery method for green liquor in paper making
11. Uses wastes as a raw material source and leaves no environmental footprint	Eliminates wastes including pathogenic ones

The embodiment of the invention in which an exclusive property or privilege is claimed are defined as follows:

- 1) An upgrading process for waste, low grade oil, petroleum crude, fats or greases comprising:
 - a) Loading feed material in the form of diverse raw materials in variable proportions with water into a pressure vessel under supercritical conditions,
 - b) Adjusting temperature and pressure in the reaction vessel to cause water to reach supercritical conditions,
 - c) Regulating and maintaining temperature / pressure in the reaction vessel for a minimal 3-10 minutes,
 - d) Isolating the array of products formed by entrapment of the gases, condensation of the liquids in an attached distillation tower and physical collection of the dry residual solids,
 - e) Entrapping carbon dioxide and amines by physical or chemical means,
 - f) Recovering energy to produce a positive energy balance, and
 - g) Separating the gaseous / liquid and solid inorganic / charred cellulosic products.
- 2) A process as described in claim 1 where diverse raw materials such as plastics, animal/vegetable protein, triglycerides and lipids in a) animal fats, b) animal excrement, and c) vegetable wastes, and resins in tar sands and petroleum heavy oil are chemically transformed into liquid hydrocarbon fuels,
- 3) A process according to claim 1 where very heavy crude is doctored with waste animal and / or vegetable oils to reduce viscosity so that a more easily pipelineable mixture is formed,
- 4) A process according to claim 1 where extra water may or may not be required as solvent,
- 5) A process as described in claim 1 where carbon dioxide and amines are recovered by physical absorption /adsorption /desorption, condensation, crystallization and chemical precipitation to reduce odour,
- 6) A process as described in claim 1 where amides in plastics such as nylon and animal / vegetable protein, where esters in polyester, and where animal / vegetable esters in triglycerides / lipids, and where resins in tar sands and petroleum heavy oil are hydrolyzed into acids, alcohols, amino acids, ammonia and amines,
- 7) A process as described in claim 6 where both free and generated acids are decarboxylated to carbon dioxide and "one carbon less" hydrocarbon,
- 8) A process as described in claim 6 where amino acids are oxidatively decarboxylated to ammonia, carbon dioxide and "one carbon less" aldehyde,
- 9) A process as described in claim 7 where decarboxylation of emulsion generating carboxylic acids causes partition of oil into separated hydrocarbon and aqueous phases,

- 10) A process as described in claim 1 where carbon-carbon and carbon-sulfur bonds in natural and synthetic polymers, oligomers, and natural petroleum waxes are reductively cleaved to generate lower molecular weight hydrocarbons and thiols,
- 11) A process as described in claim 1 where tramp metals such as vanadium, nickel and iron precipitate out because lower molecular weight hydrocarbons cannot solubilize them,
- 12) A process as described in claim 2 where amines, both added and generated act as catalysts in the hydrolysis of amides, esters, and thioesters,
- 13) A process as described in claim 12 where amines, both added and generated inhibit the corrosive nature of water at supercritical temperatures,
- 14) A process as described in claim 1 where iron oxide, sulfide ion and carbonate ion are catalysts,
- 15) A process as described in claim 1 where the reactions are simultaneously occurring independently, in concert and in cascade fashion,
- 16) A process as described in claim 1 where reactions occur in 3-10 minutes,
- 17) A process as described in claim 5 where hydrolysis and decarboxylation occur at a temperature of 200-430.degree.C,
- 18) A process as described in claim 1 where carbon-carbon and carbon-sulfur scission occurs at a temperature of 430-500.degree.C,
- 19) A process as described in claim 4 where super critical water reductively hydrogenates the cleaved carbon-carbon and carbon-sulfur terminal radicals without generating coke,
- 20) A process as described in claim 1 where super critical water with a dielectric constant of $\psi = 2-5$ is miscible with hydrocarbons,
- 21) A process as described in claim 1 where generated carbon dioxide is precipitated by lime water and amines are trapped as ammonium salts,
- 22) A process as described in claim 5 where socially unacceptable amine odours are controlled by transforming them into ammonium salts,
- 23) A process as described in claim 1 where animal and vegetable derived pathogens are destroyed by sterilization at super critical temperatures and pressures,
- 24) A process as described in claim 1 where the inorganic and poly saccharide fractions of animal/vegetable waste become nitrogen depleted carbonaceous compost,
- 25) A process as described in claim 2 where a mixture of petroleum and triglycerides generates glycerol that desiccates the hydrocarbon phase,

- 26) A process where black liquor need not be concentrated in order to separate chemically solubilized lignin from the aqueous phase,
- 27) A process as described in claim 26 that causes chemically solubilized wood extracted lignin to be chemically transformed into non-aqueous soluble liquid hydrocarbon and solid carbonaceous fuel.
- 28) A process as described in claim 26 where sulfide catalyst and Kraft sulfide ions respectively are oxidized into sulfate ion,
- 29) A process where heavy crude petroleum and used lubricating oils can be demineralized, decolourized and dried in one step, and finally
- 30) A process as described in claims 1 and 26 where 50-70% of the heat from the post-reaction cool down process steps is recycled to the pre-reaction raw materials.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CA 01/00780

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G1/04 C10G1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 02977 A (MITSUBISHI HEAVY IND LTD ;TOHOKU ELECTRIC POWER CO (JP)) 20 January 2000 (2000-01-20) abstract	1, 2, 4, 6, 13, 15, 19, 20, 22-25
X	WO 81 00855 A (MODAR INC) 2 April 1981 (1981-04-02) claims 1, 4-7, 17, 18 page 3, line 23 - line 26 page 4, line 29 - line 35 page 5, line 16 - line 19 page 6, line 24 - page 7, line 1	1, 4, 6-13, 15-17, 19, 20, 22-25

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
 E earlier document but published on or after the international filing date
 L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 O document referring to an oral disclosure, use, exhibition or other means
 P document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
 Z document member of the same patent family

Date of the actual completion of the international search

28 June 2002

Date of mailing of the international search report

04/07/2002

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Authorized officer

De Herdt, 0

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CA 01/00780

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 002 767 A (CENTER FOR COAL UTILIZATION ;JAPAN AS REPRESENTED BY DIRECT (JP)) 24 May 2000 (2000-05-24) claims 1,2,5 ---	1,4-15, 19,20, 22-25
X	DE 44 11 483 A (YAMASAKI NAKAMICHI ;NISHIKAWA RUBBER CO LTD (JP)) 6 October 1994 (1994-10-06) page 1, line 6 - line 8 ---	1,3,8
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X	US 4 719 000 A (BECKBERGER LAVERN H) 12 January 1988 (1988-01-12) claims 1,3,6 ---	1,4, 6-13,15, 18-20, 22-25
X	US 5 228 982 A (SCOUTEN CHARLES G ET AL) 20 July 1993 (1993-07-20) claims 1,4,12 ---	1,4, 6-13,15, 17,19, 20,22-25
X	WO 01 70917 A (RUSSELL RICHARD W ;STILLER ALFRED H (US); UNIV WEST VIRGINIA (US)) 27 September 2001 (2001-09-27) claims 1,4,12 figure 1 -----	1,4, 6-13,15, 17,19, 20,22-25

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 26-29 30(partially)

Present claims 26-29 and 30(partially) relate to a process without defining technical features. Lack of clarity within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and/or concise), namely claims 1 to 25 and 30(partially as referred to claim 1)

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA 01/00780

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 26-29 30(partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 01/00780

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